

1,4-Diazoniabicyclo[2.2.2]octane aqua-bis(oxalato- κ^2O,O')copper(II) dihydrate

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Key indicators

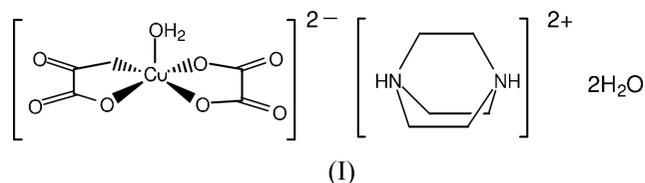
Single-crystal X-ray study
 $T = 167\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.040
 wR factor = 0.103
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$, crystallizes in the space group $P\bar{1}$. In the solid state, the $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$ units (ox is oxalate, C_2O_4) dimerize to give a tetragonally distorted CuO_6 coordination environment. Extensive hydrogen bonding between the oxalate, the coordinated water, the 1,4-diazoniabicyclo[2.2.2]octane dications ($[\text{dabcoH}_2]^{2+}$) and the water of crystallization determines the crystal packing.

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Comment

Blue crystals of the title compound, (I), were obtained by a slow diffusion technique in an aqueous gel. This ionic compound crystallizes in the triclinic space group $P\bar{1}$, with two formula units per unit cell. The structure of (I) contains $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$ (ox is oxalate, C_2O_4) units, in which the Cu^{II} ion is coordinated by two chelating oxalate ions in a planar geometry, and the coordinated water molecule forms a long axial contact $[\text{Cu1}-\text{O1W}\ 2.344(7)\text{ \AA}]$. These units dimerize through one of the coordinating O atoms of the oxalate (Fig. 1 and Table 1), resulting in a $\text{Cu1}\cdots\text{Cu1}^i$ separation of $3.818(8)\text{ \AA}$ [symmetry code: (i) $-x, 1-y, 1-z$]. The long $\text{Cu1}-\text{O3}^i$ contact of $2.906(10)\text{ \AA}$ gives an idea of the weakness of the dimerization interaction.



The number of hydrogen-bond acceptor sites in (I) is greater than the number of potential hydrogen-bond donating groups. We note that all $D-H$ groups are involved in hydrogen bonding, and that there are seven different (near) linear and one bifurcated hydrogen-bond interactions (Table 2). Neighbouring $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]_2^{4-}$ units are directly hydrogen-bonded into chains. These chains are hydrogen-bonded through the water of crystallization, resulting in an extensive three-dimensional network (Fig. 2). The unsymmetric bifurcated hydrogen bond between the oxalate and 1,4-diazoniabicyclo[2.2.2]octane ($[\text{dabcoH}_2]^{2+}$) is a motif seen in almost all other compounds containing $[\text{dabcoH}_2]^{2+}$ and ox^{2-} (Vaidhyanathan *et al.*, 2001; Lee & Wang, 1999; Malfant *et al.*, 1990), although we note that this hydrogen-bonding pattern is not uncommon in oxalate compounds.

As described previously (Keene *et al.*, 2003, 2004), discrete mono- and dinuclear metal oxalate species may be formed

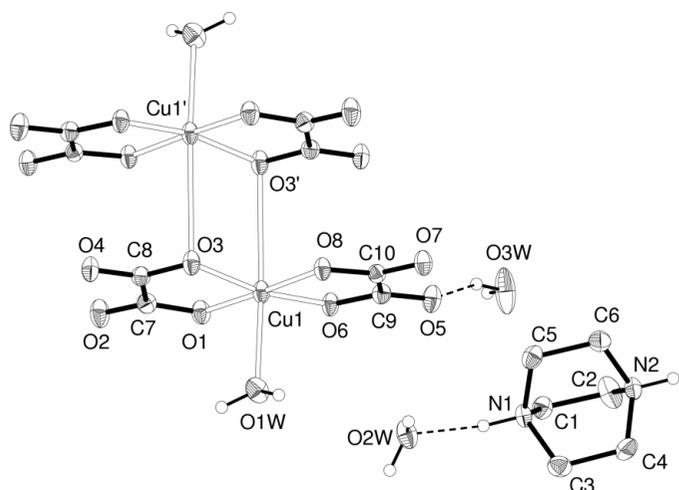


Figure 1
The asymmetric unit and selected symmetry equivalents of (I), showing the dimerization of the $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$ unit. Displacement ellipsoids are drawn at the 50% probability level. Some H atoms have been omitted for clarity. Primed atoms are generated by the symmetry operation $(-x, 1 - y, 1 - z)$.

when the bridging potential of the oxalate is reduced. This can be achieved either through the use of capping ligands or by a high concentration of the oxalate dianion, in both cases resulting in coordinatively saturated complexes. The large Jahn–Teller effect in Cu^{II} makes the structural chemistry of copper oxalate compounds different from that of other 3d transition metals. In particular, a displacement of the labile axial water molecules during crystallization is commonly observed, and a polycatenation process results in chains of $[\text{Cu}(\text{ox})_2]^{2n-}$ in the solid state. Very few examples of isolated $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$ (Insausti *et al.*, 1994; Keene *et al.*, 2004) or dimerized species (Savel'eva *et al.*, 1992) have been observed in the solid state. In the case of (I), the extensive hydrogen-bonded network stabilizes the discrete dimerization of the copper bisoxalate dianions, to give isolated $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})_2]^{4-}$ units.

Experimental

Single crystals of (I) were synthesized by a gel-crystallization technique. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg, 0.40 mmol) was dissolved in distilled water (18 ml). Tetramethoxysilane (2 ml) was added and the mixture stirred until monophasic, then allowed to set in a test tube. A solution of 1,4-diazoniabicyclo[2.2.2]octane bis(hydrogenoxalate) (200 mg, 0.68 mmol) was added to the top of the gel. After two weeks, light-blue crystals of (I) had formed in the gel. IR (KBr, diffuse reflectance, cm^{-1}): 3450 s (O–H stretch), 2823 s (C–H stretch), 2650 s (N–H stretch), 1681 s and 1658 s (oxalate), 1412 s (oxalate), 1291 s, 1059 s, 850 s, 801 s, 607 m, 540 m, 495 m; UV/VIS/NIR (diffuse reflectance, cm^{-1}): 14 400 (*d-d*), 35 700 (oxalate).

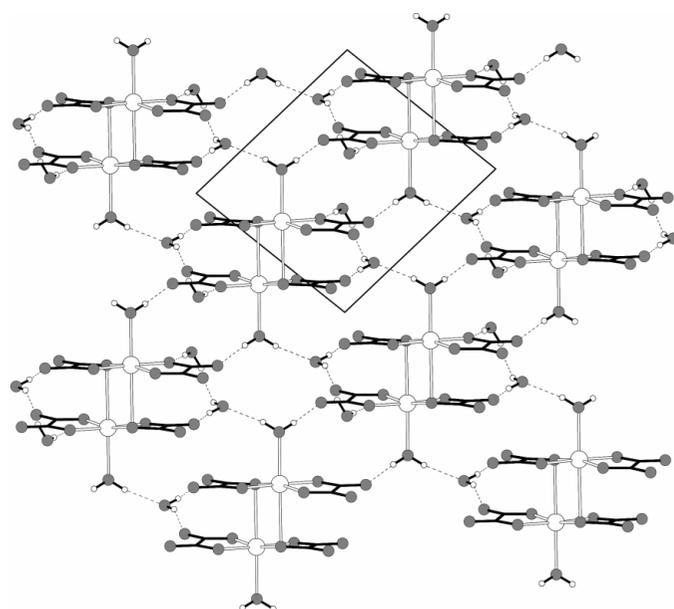


Figure 2
Hydrogen-bonding interactions (dashed lines) between $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$ clusters and the water of crystallization, viewed along the *b* axis.

Crystal data

$(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$
 $M_r = 407.82$
Triclinic, $P\bar{1}$
 $a = 9.3847$ (7) Å
 $b = 9.4884$ (6) Å
 $c = 9.6936$ (5) Å
 $\alpha = 62.150$ (4)°
 $\beta = 81.987$ (4)°
 $\gamma = 87.868$ (3)°
 $V = 755.36$ (9) Å³

$Z = 2$
 $D_x = 1.793$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 9717 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 1.51$ mm⁻¹
 $T = 167$ (2) K
Block, blue
 $0.42 \times 0.12 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1997)
 $T_{\text{min}} = 0.696$, $T_{\text{max}} = 0.886$
7866 measured reflections

3465 independent reflections
3018 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -10 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -11 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.103$
 $S = 1.05$
3465 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.8532P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.71$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O6	1.9366 (18)	Cu1—O1	1.9584 (18)
Cu1—O3	1.9458 (19)	Cu1—O8	1.9617 (17)
Cu1—O3 ⁱ	2.9058 (18)	Cu1—O1W	2.343 (2)

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O2W	0.91	1.84	2.698 (4)	157
N2—H2 \cdots O4 ⁱⁱ	0.91	1.90	2.690 (3)	144
N2—H2 \cdots O2 ⁱⁱ	0.91	2.28	2.978 (5)	133
O2W—H21 \cdots O8 ⁱⁱⁱ	0.87 (2)	1.95 (2)	2.819 (5)	178 (2)
O2W—H22 \cdots O3W ^{iv}	0.87 (2)	2.36 (2)	3.201 (4)	163 (2)
O3W—H31 \cdots O5	0.88 (4)	1.95 (4)	2.770 (6)	155 (4)
O1W—H11 \cdots O7 ⁱⁱⁱ	0.87 (3)	1.98 (3)	2.837 (5)	169 (3)
O1W—H12 \cdots O3W ^v	0.875 (18)	1.942 (19)	2.800 (6)	166.1 (16)
O3W—H32 \cdots O2 ^{vi}	0.87 (3)	1.88 (3)	2.703 (6)	157 (3)

Symmetry codes: (ii) $1+x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $x, y, z-1$; (vi) $-x, 2-y, 1-z$.

H atoms bound to C and N atoms were positioned geometrically and refined as riding, with C—H = 0.97 and N—H = 0.91 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. H atoms bound to O atoms were located in difference maps, but their distances and angles were restrained to literature values.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT* (Nonius, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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